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(54) **A composition causing different skin sensations**

(57) The present invention is directed to a sensate composition including at least one cooling sensate, warming sensate and tingling sensate. The tingling sensate is at least one of Jambu Oleoresin and Spilanthol. The present invention is further directed to a method of using the sensate composition in a food, pharmaceutical or personal care product.

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Description

[0001] The present invention relates to a composition imparting an initial sensation similar to tingling upon first contact. More specifically, the present invention is a composition including a cooling sensate, a warming sensate and a tingling-type sensate, which when used in combination, imparts an immediate initial sensation. The initial sensation can best be described as a tingling or a stinging impression which also enhances the sensation of the other sensates used in the composition. In addition, the composition of the present invention also helps moderate the harsh and stimulative effects of the cooling agents. This moderation of the harsh effects of cooling agents is referred to herein as an emollient effect.

[0002] Various types of products incorporate ingredients which impart some kind of sensation to the mucous membranes, oral cavity, throat or skin. These ingredients may be used as flavors or fragrances in a wide range of products such as personal care products (perfumes deodorants, cosmetics, shampoos, skin creams, toothpastes and the like), pharmaceuticals (such as cough syrups, cough drops and the like) and foods (such as chewing gum, soda and the like).

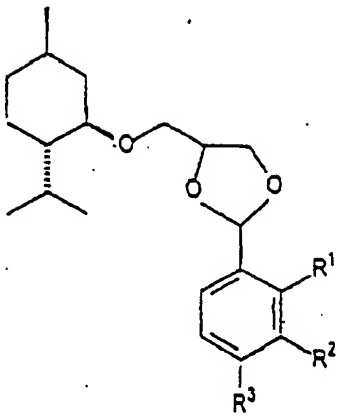
[0003] For example, ℓ-menthol and 3-(ℓ-menthoxy)propane-1,2-diol are used as active ingredients in products to impart a cooling sensation to the mouth or skin (U.S. Patent No. 4,459,425). However, ℓ-menthol has the drawback of being very volatile as well as irritating to skin and mucous membranes. There is a limit to how much ℓ-menthol can be used in a product to produce a cooling sensation, because when used in greater amounts the ℓ-menthol becomes very harsh and irritating. Much research has been done to find alternatives to menthol as a cooling agent. In *New Compounds with the Menthol Cooling Effect,* J. Soc. Cosmet. Chem., 29: 185-200 (1978), by H.R. Watson et al., the physiological basis for the cooling effect of menthol is discussed. In addition, certain important molecular requirements were described that are believed to be necessary in order for a compound to have the desired effect. Several N-alkyl-carboxamide compounds were found to possess the cooling sensation of menthol while having the advantage of being less volatile. The pharmacology and toxicology of menthol use in various products and for various modes of administration has also been reported. See *Menthol and Related Cooling Compounds,* J. Pharm. Pharmacol., 46: 618-630 (1994), by R. Eccles.

[0004] Another alternative to menthol is 1(2'-hydroxyphenyl)-4-(3'-nitrophyenyl)-1,2,3,5-tetrahydropyrimidine-2-one. This compound is discussed in *A Chemical Which Produces Sensations of Cold,* Enviromnment, Drugs and Thermoregulation, 5th International Symp. Pharmacol. Thermoregulation, Saint-Paul-de-Vence, 1982, pp. 183-186 (Karger, Basel, 1983) by E.T. Wei.

[0005] Other known physiological cooling agents including peppermint oil, N-substituted-p-menthane-3-carboxamides, acyclic tertiary and secondary carboxamides, 3-ℓ-menthoxy propan-1,2-diol have also been reported (See PCT Published Application Number WO 97/06695).

[0006] Heating and/or warming sensates are also known. Vanillyl alcohol n-butyl ether (vanillyl butyl ether) is known as an active ingredient in products to impart a sharp, tangy bite or a heating/warming sensation (Japanese Laid-Open Application No. 54-67040). A formulation for cough drops has been reported which includes a physiological cooling agent and a physiological warming agent (PCT Published Application No. 1WO 97/06695). Physiological cooling agents disclosed therein include peppermint oil, N-substituted-p-menthane-3-carboxamides, acyclic tertiary and secondary carboxamides, 3-ℓ-menthoxy propan-1,2-diol. Physiological warming agents disclosed therein include vanillyl alcohol n-butyl ether, vanillyl alcohol n-propyl ether, vanillyl alcohol isopropyl ether, vanillyl alcohol isobutyl ether, vanillyl alcohol n-amino ether, vanillyl alcohol isoamyl ether, vanillyl alcohol n-hexyl ether, vanillyl alcohol methyl ether, vanillyl alcohol ethyl ether, gingerol, shogaol, paradol, zingerone, capsaicin, dihydrocapsaicin, nordihydrocapsaicin, homocapsaicin, homodihydrocapsaicin, ethanol, iso-propyl alcohol, iso-amylalcohol, benzyl alcohol, chloroform, eugenol, cinnamon oil, cinnamic aldehyde and phosphate derivatives of same.

[0007] A compound that possesses a hot, burning and tingling taste that is long lasting has been reported as 4-(ℓ-menthoxymethyl)-2-phenyl-1,3-dioxolane or its derivatives represented by the following general formula (I):



(I)

wherein R^1 represents a hydrogen atom, a hydroxy group or a lower alkoxy group, R^2 and R^3, which may be the same or different, each represent a hydrogen atom, a hydroxy group, a lower alkoxy group, or when taken together, R2 and R3 represent a methylene dioxy group. See U.S. Patent No. 5,545,424 which is herein incorporated by reference. This warming sensate was also reported to prolong the sensations of certain cooling sensates, for example in combination with 1-menthol, 3-(ℓ-menthoxy)propan-1,2-diol («TK-10" by Takasago International Corp., Tokyo, Japan) or isopulegol. The combination of the cooling and warming sensates signaled prolonged cooling effects to the user. Thus, the burning, tingling or bitter sensations associated with this warming sensate were able to convey to the user a better appreciation of the cooling sensate.

[0008] In addition, vanillyl alcohol n-butyl ether (vanillyl butyl ether) is known as an active ingredient in products to impart a sharp, tangy bite or a heating/warming sensation (Japanese Laid-Open Application No. 54-67040 and Examined Japanese Patent Application No. 61-9293).

[0009] Certain materials are known to cause a tingling, numbing and/or stinging sensation and are used in foods as popular spice and/or herb condiments. These include Jambu Oleoresin or para cress (*Spilanthes sp.*) the active ingredient being Spiranthol; Japanese pepper extract (*Zanthoxylum peperitum*) having the active ingredient(s) known as Saanshool-I, Saanshool-II and Sanshoamide; Black pepper extract (*Piper nigrum*) having the active ingredients Chavicine and Piperine.

[0010] It is also known to combine compounds known to possess flavor and/or sensate compounds to produce new active ingredients having altered properties. For example, PCT published application WO 98/47482 discloses formulations for cough drops which include a physiological cooling agent (such as menthol, peppermint oil, n-N-substituted-p-menthane-3-carboxamides, acyclic tertiary and secondary carboxamides, 3-(ℓ-menthoxy)propan-1,2-diol and a physiological warming agent (such as vanillyl alcohol n-butyl ether, vanillyl alcohol n-propyl ether, vanillyl alcohol isopropyl ether, vanillyl alcohol isobutyl ether, vanillyl alcolol n-amino ether, vanillyl alcohol isoamyl ether, vanillyl alcohol n-hexyl ether vanillyl alcohol methyl ether, vanillyl alcohol ethyl ether, gingerol, shogaol, paradol, zingerone, capsaicin, dihydrocapsaicin, nordihydrocapsaicin, homocapsaicin, homodihydro-capsaicin, ethanol, iso-propyl alcohol, iso-amylalcohol, benzyl alcohol, chloroform, eugenol, cinnamon oil, cinnamic aldehyde and phosphate derivatives of same.

[0011] Use of vanillyl butyl ether in combination with a cooling agent is disclosed in co-pending application entitled «COOL FEELING COMPOSITION» filed on or about August 4, 1999 by one or more of the inventors of the present invention. The composition disclosed therein imparts a refreshing sensation in various consumer products.

[0012] The known cooling, warming and combination sensate compounds tend to have a lag time between first contact and when the sensate is first detected. It is often seconds before the sensation is actually perceived by the user. In addition, the cooling and warming sensate compounds, and combinations thereof that are known to date, do not last very long. It is often only a few seconds or minutes before the sensation wanes. It is desirable to have a cooling, warming or combination sensate compound that is perceived by the user immediately upon first contact with the user. It is also desirable for the perceived sensation to last for a greater duration of time than just the first few seconds or so.

[0013] It is an object of the present invention to provide a taste and touch sensate that overcomes the limitations of the prior art.

[0014] It is an object of the present invention to provide a sensate compound that provide a strong initial signal to the user.

[0015] It is a further object of the present invention to provide a sensate compound that provides a tingling and/or stinging impression upon contact.

[0016] It is a further object of the present invention to provide a sensate compound that provides lasting sensation

beyond first contact.

[0017] It is a further object of the present invention to provide a sensate compound that provides an emollient effect on one or more stimulative co-ingredients.

[0018] After extensive research, the inventors of the present invention have discovered that combining cooling sensates with warming sensates and a tingling sensate (such as Jambu oleoresin or Spilanthol), results in enhancement of the flavor and/or sensation of the cooling and/or warming sensates. In addition, this combination has been shown to initiate perception of the flavor of the sensates in a shorter period of time than occurs when either the cooling sensate, the warming sensate, or a combination of the two are used without the tingling sensate.

[0019] Briefly stated, the present invention relates to a sensate composition including at least one cooling sensate, at least one warming sensate and at least one tingling sensate.

[0020] To this end, there is provided a sensate composition, comprising:

a cooling sensate, wherein the cooling sensate imparts at least one of the sensations selected from the group consisting of cold, cooling, chilly and fresh, when present on skin, mucous membranes, mouth or throat;
a warming sensate, wherein the warming sensate imparts at least one of the sensations selected from the group consisting of heat, warming, burning, scorching, sizzling, baking and searing when present on skin, mucous membranes, mouth or throat; and
a tingling sensate, wherein the tingling sensate imparts at least one of the sensations selected from the group consisting of tingling, tickly, itchy, scratchy pungent and stinging when present on skin, mucous membranes, mouth or throat.

[0021] Preferably, each of the cooling sensate, the warming sensate and the tingling sensate are from about 0.001% by weight to about 20% by weight of the sensate composition.

[0022] Preferably yet, each of the cooling sensate, the warming sensate and the tingling sensate are from about 0.01 % by weight to about 15 % by weight of the sensate composition.

[0023] Preferably further, each of the cooling sensate, the warming sensate and the tingling sensate are from about 0.01 % by weight to about 12 % by weight of said sensate composition.

[0024] Typically, the cooling sensate is at least one of menthol, isopulegole, 3-(ℓ-menthoxy)propan-1,2-diol, p-menthan-3,8-diol, 6-isopropyl-9-methyl-1,4-dioxaspiro-(4,5)-decane-2-methanol, menthyl succinate and alkaline earth salts thereof, trimethyl cyclohexanol, N-ethyl-2-isopropyl-5-methylcyclohexane carboxamide, 3-(ℓ-menthoxy)-2-methyl-propan-1,2-diol, mint oil, peppermint oil, wintergreen, menthone, menthone glycerin ketal, menthyl lactate, (1'R, 2'S,5'R)-2-[5'methyl-2'-(methylethyl)cyclohexyloxy]ethan-1-ol, (1'R,2'S,5'R)-3-[5'methyl-2'-(methylethyl)cyclohexyloxy)]propan-1-ol, (1'R,2'S,5'R)-4-[5'-methyl-2'-(methylethyl)cyclohexyloxy]butan-1-ol or spearmint.

[0025] Typically yet, the warming sensate is at least one of the group consisting of vanillyl ethyl ether, vanillyl propyl ether, vanillin propylene glycol acetal, ethyl vanillin propylene glycol acetal, capsaicin, gingerol, vanillyl butyl ether, 4-(ℓ-menthoxymethyl)-2-phenyl-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(3',4'-dihydroxyphenyl)-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(2'-hydroxy-3'-methoxyphenyl)-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(4'-methoxyphenyl)-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(3,'4'-methylenedioxyphenyl)-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(3'-methoxy-4'-hydroxyphenyl)-1,3-dioxolane, hot pepper oil, capsicum oleoresin, ginger olioresin and nonyl acid vanillylamide.

[0026] Typically further, the tingling compound is at least one of the group consisting of Jambu Oleoresin, Japanese pepper extract (*Zanthoxylum peperitum*), saanshool-I, saanshool II, sanshoamide, black pepper extract (*Piper nigrum*), chavicine, piperine and Spilanthol.

[0027] Further in the present invention, the cooling sensate may be from about 0.01 % by weight to about 20 % by weight of the composition, independently from the other sensate compounds involved.

[0028] Likewise, the warming sensate may be from about 0.01 % by weight to about 20 % by weight of the composition.

[0029] Likewise yet, the tingling sensate may be from about 0.01 % by weight to about 20 % by weight of the composition.

[0030] There is also provided a method of using a sensate composition as at least one of a fragrance or a flavor, comprising:

forming a sensate composition having at least one cooling sensate, at least one warming sensate and at least one tingling sensate containing effective amounts of the sensates; and
admixing the sensate composition with a suitable carrier.

[0031] The method may further comprise admixing the composition with appropriate adjunct ingredients to form a product, whereby the product is effective to act as at least one of a personal care product, a food and a pharmaceutical.

[0032] The above personal care product may be selected from the group consisting of a soap, a deodorant, a antiperspirant, a skin lotion, a skin cream, a moisturizer and an ointment.

[0033] Likewise, the above food may be selected from the group consisting of a candy, a lozenge, a confectionary, a chewing gum, a mint, a chocolate, a cake, a cookie, a beverage, an alcoholic b verage, a seasoning, a salad dressing, and a dip.

[0034] Further, the above pharmaceutical may be selected from the group consisting of a topical medicine, a nebulizer, a medicated lozenge and a chewable medicine.

[0035] In an embodiment of the present invention, a method of using a sensate composition as at least one of a fragrance and a flavor is provided, which includes forming a sensate composition having at least one cooling sensate, at least one warming sensate and at least one tingling sensate containing effective amounts of the sensates and admixing the sensate composition with a suitable carrier.

[0036] The above, and other objects, features and advantages of the present invention will become apparent from the following description. However, these examples are not to be construed to limit the scope of the invention.

[0037] As described above, ℓ-menthol, 3-(ℓ-menthoxy)propan-1,2-diol and other compounds are known cooling agents. In addition, vanillyl butyl ether is known as a warming sensate. Jambu oleoresin is an extract used to impart tingling flavor in foods.

[0038] In the new sensate of the present invention, vanillyl butyl ether is combined with a cooling sensate and a warming sensate to impart an immediate sensation upon contact that also provides an emollient effect on the cooling sensate. The cooling sensate can be a single cooling sensate or a combination of different cooling sensates. The warming sensate can be a single such sensate or a combination thereof.

[0039] There are no specific limitations to the relative amounts of the compounds of the composition. However, it is preferred that vanillyl butyl ether is used in a relative amount with respect to the cooling agent so that no discernable warming effect occurs. Preferably, vanillyl butyl ether is used on a weight basis, from 1/1000 to 2 times as much as the cooling agent. More preferably, the vanillyl butyl ether is present in the composition from 1/200 to 1 time the amount of the cooling agent on a weight basis.

[0040] The new sensate composition of the present invention may further contain diluents (ethanol, purified water, etc.) which are safe for use in products used for consumption and/or topical use. The new sensate composition of the present invention can be used in various products to which the qualities of the sensate are desirable. Examples of suitable products include: cosmetics (such as lipstick, after shave lotions, foundation and the like), personal care products (such as skin creams, astringent lotions, cleansing lotions, deodorants, shampoos, conditioners, soaps, hair. gels, hair tonics, hair growth stimulants, shaving foams, shaving creams, bubbling bath beads and the like) and pharmaceutical compositions (such as insect repellent sprays, hair tonics, analgesic preparations, lozenges and the like). These are set forth as examples, however the products in which the composition of the present invention may be used are not limited to these.

[0041] The amount of the sensate composition of the present invention in a product varies widely depending on the amount of the product used at one time and the manner in which it is used or applied. In general, the content of the sensate composition may be from 0.001 to 20 % by weight, preferably from 0.01 to 15 % by weight of the entire product composition. However, the sensate composition may be added to a product in any amount, as long as the effect of the composition is present. The sensate composition may be made first, then added to a product. Alternatively, the cooling agent, warming agent and tingling agent may be added separately to the product.

[0042] The present invention will be described in greater detail by reference to the following Embodiments and Comparative Examples, however, it should be noted the invention is not limited to these examples.

Embodiment 1 (E1)

[0043] Embodiment 1 was prepared by mixing N-ethyl-2-isopropyl-5-methylcyclohexane carboxamide (3.0 wt %) and isopulegole (8.0 wt %) as cooling agents, vanillyl butyl ether (3.0 wt %) as a warming agent and Jambu Oleoresin (2.5 wt %) as a tingling agent with other ingredients according to the following formulation to produce a mouthwash. These ingredients are prepared according to methods that are known in the art.

Ingredient	% by weight in flavors
ethyl alcohol	55.0
propylene glycol	28.0
N-ethyl-2-isopropyl-5-methylcyclohexane carboxamide	3.0
isopulegole	8.0

(continued)

Ingredient	% by weight in flavors
Jambu Oleoresin	2.5
vanillyl butyl ether	3.0
mouthwash herbal flavor base	0.5

[0044] A sensory evaluation was performed on the mouthwash of Embodiment 1. Eight members of a panel trained as Flavorists evaluated the products. They found that the blend produced a unique flavor and taste profile. Members of the panel reported a tingling sensation upon first contact with the mouthwash. No delay in perceived sensation was reported.

Comparative Example 1 (CE1)

[0045] Comparative Example 1 was made in the same manner as Embodiment 1, except that Jambu Oleoresin was omitted.

[0046] A taste panel was convened to evaluate any perceived differences in character between the mouthwash of Embodiment 1 and Comparative Example 1. Panelists were asked to compare the flavor sensation of the two products and comment on any differences.

[0047] The majority of the panelists noted that there was a distinct difference in warming sensation perception and onset. The coded sample containing the Jambu Oleoresin was described as having a fuller warming, tingling effect as compared to the Jambu free system which was less complex and less stimulating with an almost retarded onset of the cooling perception. There was a noted synergistic effect between the ingredients. The profiles were described as a significant tingling and an enhancement of the cooling and warming perception of the product. The study showed that all three components, cooling, heating and tingling are necessary to produce the observed unique effect.

Embodiment 2 (E2)

[0048] Embodiment 2 was prepared by mixing 3-(ℓ-menthoxy)propan-1,2-diol («TK-10" from Takasago, Takasago International Corp., Tokyo, Japan) as a cooling agent (2.0 wt %), capiscum oleoresin (0.5 wt %) and ginger oleoresin (2.0 wt %) as warning agents and Jambu Oleoresin (10 wt %) as a tingling agent with other ingredients according to the following formulation to make a toothpaste according to methods that are known in the art.

Ingredient	% by weight
ethanol	51.5
Benzyl alcohol	34.0
Jambu Oleoresin	10.0
Ginger Oleoresin	2.0
Capsicum Oleoresin	0.5
3-(ℓ-menthoxy)propan-1,2-diol (<<TK-10")	2.0

Comparative Example 2 (CE2)

[0049] Comparative Example 2 was prepared in the same manner as Embodiment 2, except Jambu Oleoresin was omitted.

[0050] A select taste panel evaluated the perceived differences in character between the toothpaste preparation of Embodiment 2 and Comparative Example 2. Panelists were asked to compare the flavor sensation of the two products and comment on any differences. Evaluations were performed blind.

[0051] The majority of the panelists noted that the sample containing the tingling sensate material had quicker tingling sensation onset and an enhanced, prolonged cool, tingling, pleasant aftertaste. Panelists for the most part perceived Comparative Example 2 to be pleasant but lacking in the robustness and impact of Embodiment 2.

Embodiment 3 (E3)

[0052] Embodiment 3 was prepared by mixing menthol (1.0 wt %) as a cooling agent, 4-(ℓ-menthoxymethyl)-2-(3'-methoxy-4'-hydroxyphenyl)-1,3-dioxolane (4.0 wt %), ginger oleoresin (3.1 wt %), vanillyl butyl ether (7.5 wt %) and capsicum oleoresin (0.1 wt %) as warming agents, and Jambu Oleoresin ((3.0 wt %) as a tingling agent, with other ingredients according to the following candy formulation which was prepared in accord with methods well known in the art.

Ingredient	% by weight
medium chain triglycerides	81.3
vanillyl butyl ether	7.5
ginger oleoresin	3.1
capsicum oleoresin	0.1
4-(ℓ-menthoxymethyl)-2-(3 '-methoxy-4'-hydroxyphenyl)-1,3-dioxolane	4.0
menthol	1.0
Jambu Oleoresin	3.0

Comparative Example 3 (CE3)

[0053] Comparative Example 3 was prepared in the same manner as Embodiment 3, except no Jambu Oleoresin was used.

[0054] A panel group was convened to evaluate Embodiment 3 and Comparative Example 3 in random blind fashion and comment on any noted differences. Eight members of a panel trained as Flavorists evaluated the product. Members of the panel reported a tingling sensation upon first contact with the candy. No delay in perceived sensation was reported. Analysis of panelists comments showed a marked enhancement of the warming sensation was realized in Embodiment 3 as compared to Comparative Example 3. The onset of the flavor was more pronounced in Embodiment 3 than in Comparative Example 3. Panelists observed Comparative Example 3 seemed to be less bright and slower to exhibit any unique sensations.

Embodiment 4 (E4)

[0055] Embodiment 4 was prepared by mixing menthol (0.5 wt %) and 3-(ℓ-menthoxy)propan-1,2-diol (0.5 wt %) as cooling agents, vanillyl butyl ether (0.05 wt %) as a warming agent and Jambu oleoresin (0.5 wt %) as a tingling agent, with other ingredients according to the following formulation. A cosmetic cologne or other similar product may be prepared from this formulation by admixture with known ingredients in accord with formulations well known in the art.

Comparative Example 4 (CE4)

[0056] Comparative Example 4 was made in the same fashion as Embodiment 4, except that Jambu Oleoresin was omitted.

Comparative Example 5 (CE5)

[0057] Comparative Example 5 was made in the same fashion as Embodiment 4, except that vanillyl butyl ether was omitted.

Ingredient	Amount (% by weight)		
	E 4	CE 4	CE 5
menthol	0.50	0.50	0.50
3-(ℓ-menthoxy) propan-1,2-diol	0.50	0.50	0.50
Vanillyl butyl ether	0.05	0.05	----

(continued)

Ingredient	Amount (% by weight)		
	E 4	CE 4	CE 5
Jambu extract (10% solution)	0.50	----	0.50
Ethanol (50% solution)	98.45	98.95	98.50

[0058] A formal panel evaluated Embodiment 4 and Comparative Examples 4 and 5 according to the following protocol. 0.1 ml of the composition was placed on a patch cloth and applied to the forearm of each of the panelists. The sensate compositions were evaluated for their relative performance in the following categories: cooling sensate, stimulation, emollient and comfort/preference. The results are reported in Table 1.

Table 1

Panellst (A-C) and Time Course	Cooling Sensate	Stimulation	Emollient	Comfort/ Preference
0 minutes				
A	CE4 > E4 > CE5	CE4 > E4 > CE5	CE5 > E4 > CE4	E4 > CE5 = CE4
B	E4 = CE4 > CE5	CE4 > E4 > CE5	CE5 = E4 > CE4	E4 > CE5 > CE4
C	E4 = CE4 > CE5	CE4 > E4 > CE5	CE5 > E4 > CE4	E4 > CE4 > CE5
5 minutes				
A	CE4 > E4 > CE5	CE4 > E4 > CE5	CE5 > E4 > CE4	E4 3 CE4 > CE5
B	E4 = CE4 > CE5	CE4 > E4 > CE5	CE5 = E4 > CE4	E4 > CE5 > CE4
C	E4 = CE4 > CE5	CE4 > E4 > CE5	CE5 > E4 > CE4	E4 > CE4 > CE5
10 minutes				
A	CE4 > E4 > CE5	CE4 > E4 > CE5	CE5 > E4 > CE4	E4 > CE5 = CE4
B	CE4 > E4 > CE5	CE4 > E4 > CE5	CE5 = E4 > CE4	E4 ∃ CE4 > CE5
C	E4 > CE4 = CE5	CE4 > E4 > CE5	CE5 = E4 > CE4	E4 > CE4 = CE5

[0059] The results showed that the addition of Jambu Oleoresin increased the emollient effect on menthol and vanillyl butyl ether without losing cooling effect. Almost all panelists preferred Embodiment 4 over Comparative Examples 4 and 5.

Claims

1. A sensate composition, comprising:

   a cooling sensate, wherein said cooling sensate imparts at least one of the sensations selected from the group consisting of cold, cooling, chilly and fresh, when present on skin, mucous membranes, mouth or throat;
   a warming sensate, wherein said warming sensate imparts at least one of the sensations selected from the group consisting of heat, warming, burning, scorching, sizzling, baking and searing when present on skin, mucous membranes, mouth or throat; and
   a tingling sensate, wherein said tingling sensate imparts at least one of the sensations selected from the group consisting of tingling, tickly, itchy, scratchy pungent and stinging when present on skin, mucous membranes, mouth or throat.

2. A sensate composition according to claim 1, wherein each of said cooling sensate, said warming sensate and said tingling sensate are from about 0.001% by weight to about 20% by weight of said sensate composition.

3. A sensate composition according to claim 1, wherein each of said cooling sensate, said warming sensate and said

tingling sensate are from about 0.01 % by weight to about 15 % by weight of said sensate composition.

4. A sensate composition according to claim 1, wherein each of said cooling sensate, said warming sensate and said tingling sensate are from about 0.01 % by weight to about 12 % by weight of said sensate composition.

5. The sensate composition according to any one of claims 1 to 4, wherein said cooling sensate is at least one of menthol, isopulegole, 3-(ℓ-menthoxy)propan-1,2-diol, p-menthan-3,8-diol, 6-isopropyl-9-methyl-1,4-dioxaspiro-(4,5)-decane-2-methanol, menthyl succinate and alkaline earth salts thereof, trimethyl cyclohexanol, N-ethyl-2-isopropyl-5-methylcyclohexane carboxamide, 3-(ℓ-menthoxy)-2-methyl-propan-1,2-diol, mint oil, peppermint oil, wintergreen, menthone, menthone glycerin ketal, menthyl lactate, (1'R,2'S,5'R)-2-[5'methyl-2'-(methylethyl)-cyclohexyloxy]ethan-1-ol, (1'R,2'S,5'R)-3-[5'methyl-2'-(methylethyl)-cyclohexyloxy)]propan-1-ol, (1'R,2'S,5'R)-4-[5'-methyl-2'-(methylethyl)-cyclohexyloxy]butan-1-ol or spearmint.

6. The sensate composition according to any one of claims 1 to 5, wherein said warming sensate is at least one of the group consisting of vanillyl ethyl ether, vanillyl propyl ether, vanillin propylene glycol acetal, ethyl vanillin propylene glycol acetal, capsaicin, gingerol, vanillyl butyl ether, 4-(ℓ-menthoxymethyl)-2-phenyl-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(3',4'-dihydroxyphenyl)-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(2'-hydroxy-3 '-methoxyphenyl)-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(4'-methoxyphenyl)-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(3,'4'-methylenedioxyphenyl)-1,3-dioxolane, 4-(ℓ-menthoxymethyl)-2-(3'-methoxy-4'-hydroxyphenyl)-1,3-dioxolane, hot pepper oil, capsicum oleoresin, ginger olioresin and nonyl acid vanillylamide.

7. The sensate composition according to any one of claims 1 to 6, wherein said tingling compound is at least one of the group consisting of Jambu Oleoresin, Japanese pepper extract (*Zanthoxylum peperitum*), saanshool-I, saanshool II, sanshoamide, black pepper extract (*Piper nigrum*), chavicine, piperine and Spilanthol.

8. The sensate composition according to claim 1, wherein said cooling sensate is from about 0.01 % by weight to about 20 % by weight of said composition.

9. The sensate composition according to claim 1, wherein said warming sensate is from about 0.01 % by weight to about 20 % by weight of said composition.

10. The sensate composition according to claim 1, wherein said tingling sensate is from about 0.01 % by weight to about 20 % by weight of said composition.

11. A method of using a sensate composition as defined in any one of claims 1 to 10 as at least one of a fragrance or a flavor, comprising:

forming a sensate composition having at least one cooling sensate, at least one warming sensate and at least one tingling sensate containing effective amounts of said sensates; and
admixing said sensate composition with a suitable carrier.

12. A method according to claim 11, further comprising admixing said composition with appropriate adjunct ingredients to form a product, whereby said product is effective to act as at least one of a personal care product, a food and a pharmaceutical.

13. A method according to claim 12, wherein said personal care product is selected from the group consisting of a soap, a deodorant, a antiperspirant, a skin lotion, a skin cream, a moisturizer and an ointment.

14. A method according to claim 12, wherein said food is selected from the group consisting of a candy, a lozenge, a confectionary, a chewing gum, a mint, a chocolate, a cake, a cookie, a beverage, an alcoholic beverage, a seasoning, a salad dressing, and a dip.

15. A method according to claim 12, wherein said pharmaceutical is selected from the group consisting of a topical medicine, a nebulizer, a medicated lozenge and a chewable medicine.

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GC/MS investigations of the minor constituents of *Piper guineense* stem

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Chemical investigations by GC/MS-analysis of stem extracts of *Piper guineense* resulted in the detection and identification of thirty-nine new constituents of the stem, apart from previously isolated constituents. These are isobutyl, pyrrolidyl and piperidyl amide alkaloids. Fifteen new natural products have been identified. Four of these natural products have been designated *iyeremide* A and B (these are pyrrolidine and piperidine analogues of *pellitorine*) and *cycloguineense* A and B, which are also piperidine analogues of cyclostachine A and B. There is a need to confirm the structures of some of these new constituents by synthesis. Apart from these amide alkaloids, many volatile oil components-monoterpenes, sesquiterpenes, terpenoids, lignans and sterols – were detected.

1. Introduction

Piper guineense Schum and Thonn, Piperaceae, is a rain forest woody climber found in the southern parts of Nigeria where it usually grows as a tree-top canopy. It is known as "iyere" in south-western Nigeria. The plant has also been reported [1] in other parts of West and central Africa particularly in Ghana and Cameroon. The plant has a reputation for its medicinal values – the leaves, fruits and roots are ingredients in herbal drug preparations for coughs, colds, bronchitis, venereal diseases, intestinal disorders, tooth-ache, rheumatism, skin problems and insect infestation. The leaves and fruits are eaten and have been used as condiments, flavorants and generally as spices in foods. The sharp peppery taste of the fruit has contributed to its acceptability and use in some food and drug preparations.

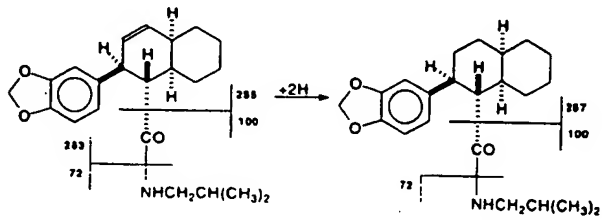
Previous chemical studies of the plant whole stem and roots have resulted in the isolation and identification of novel amide alkaloids [2–5]. This present work was undertaken to examine the chemical constituents of the stem, a part that has not been examined thoroughly before.

2. Investigations, results and discussion

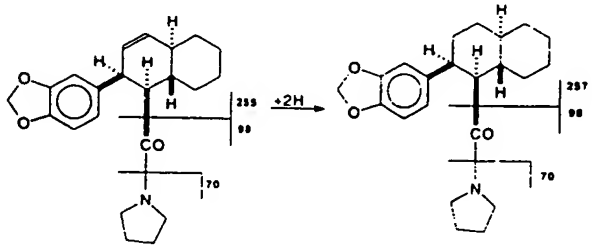
On GC/MS examination the pulverized stem pentane extract revealed the presence of some monoterpene hydrocarbons (characterized by 9 or more peaks at mass units 134, 136, identified as pinene, *p*-cymene, limonene, phellandrene etc.), sesquiterpene hydrocarbons and alcohols or ketones (characterized by 36 or more peaks at mass units 204, 220, 222, identification-MS library-elemene, copaene, guaiene, caryophyllene, cadinene and their derivatives etc.) and free fatty acids which were eluted from the column within the first 45 min of the programme. Eluted along with these volatile oil constituents were benzoic acid (GC_{tR} = 17.66 min, M^+ 122), thymol (GC_{tR} = 27.90 min, M^+ 150), piperonal (GC_{tR} = 25.06, M^+ 150), vanillin (GC_{tR} = 27.90 min, M^+ 152), 3,4-methylenedioxybenzoic acid (GC_{TR} = 32.69 min, M^+ 166) and the more volatile amide alkaloids.

A list of 51 amide alkaloids identified includes 18 isobutylamides, 14 pyrrolidides and 19 piperidides. The identification was made easier because these amides are well-suited to GC-MS analysis – the amides are well separated on the 30 m long column and MS provides enough structural information to permit the deduction of structures of interest.

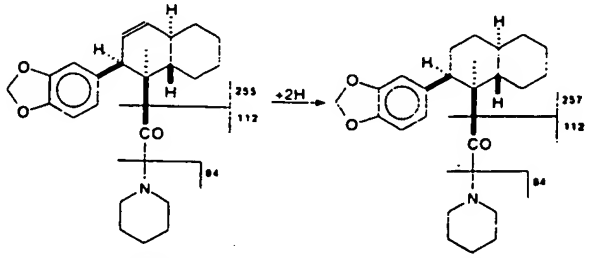
For all the compounds, both aliphatic and aromatic, prominent and significant peaks in the MS could be accounted for with fragmentation at the N–CO bond followed by cyclisation, fissions and hydrogen transfers as noted earlier [4, 7, 8]. All compounds gave parent ions. This is particularly important for the *Piper trichostachyon* alkaloids **17**, **29**, and **31**. The MS fragmentation observed for cyclopiperstachine (**17**), cyclostachine (**29**) and the new natural product, cycloguineense **B** (**51**) and their hydrogenated products can be rationalized, following the scheme of Joshi et al. [9]. The major ions for **51** and its enantiomer, cycloguineense **A** (**50**) occurred at m/z 255,



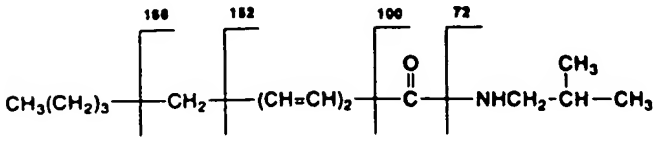
17, m/z=355 m/z = 357



29, m/z = 353 m/z = 355



51, m/z = 367 m/z = 369



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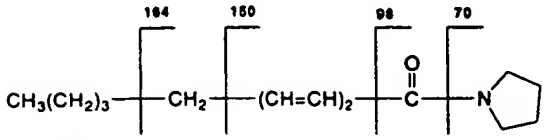

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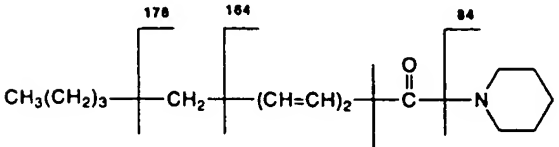
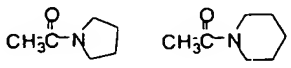


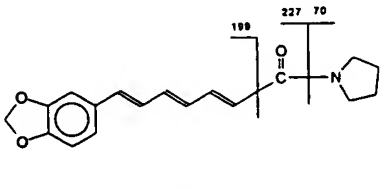
36

232, 135 and 112. Piperine (**46**), wisanine (**48**), piperlonguminine (**16**), trichostachine (**25**), the isobutylamides and their derivatives are well-known and their fragmentation patterns are well understood. Compounds with pyrrolidyl and piperidyl moieties in their molecules also offer neat fragmentation patterns for the recognition of the moieties in their spectra.

This work represents a first report of the occurrence of pyrrolidine and piperidine analogues of pellitorine in nature for which we are proposing the trivial names *iyeremide* A for *N*-pyrrolidyl-2,4-decadienamide (**20**) and *iyeremide* B for *N*-piperidyl-2,4-decadienamide (**36**) because of their structural relationship to pellitorine (**3**) [11], the well-known pungent and insecticidal component of *Anacyclus*



19 33



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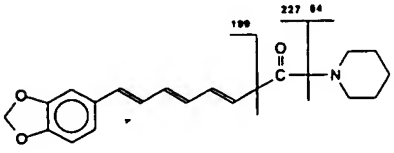

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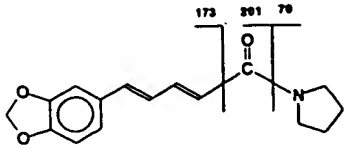

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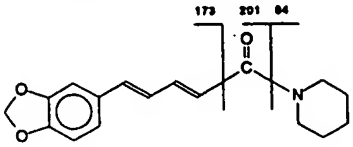

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pyrethrum. Of special interest also are the small molecules **19** and **33** which are also new natural products and, whose structures we have confirmed by synthesis. *Piper guineense* has also furnished 1-piperettyl pyrrolidine (**32**) the higher homologue of trichostachine (**25**) and piperettine (**49**), the higher homologue of piperine (**46**) earlier isolated from *Piper nigrum* [12].

3. Experimental

3.1. General procedures

Melting points were uncorrected. NMR (^1H, ^{13}C) experiments were recorded in $CDCl_3$ on a Gemini 200 MHz using TMS as an internal standard and chemical shifts are shown as δ-values (ppm). MS (as direct inlet, EI at 70 eV, ion source at 200 °C) were recorded as m/z (rel. int) on a FINNIGAN MAT instrument, Model GCQ-Mass spectrometer, serial No GQ 200037 fitted with Model GCQ-Gas chromatography and on a J & W Scientific high resolution GC column, DB-5, 30 metres long with I.D (mm), 0.25, film (μm) 0.25, serial No US 1402756H. Carrier gas He: 10 psi-20 psi with conditions: T_1, 50 °C (2 min), programme 3 °C/min until T_2, 270 °C (30 min). TLC was carried out using silica gel 60 F_{254} (Merck) and solvents for TLC were I, Tol./EtOAc (4 + 1), II, Tol./EtOAc (1 + 1) and (III), $CHCl_3$/MeOH (9 + 1); detection: UV-light. IR spectra were recorded as KBR pellets.

3.2. Plant material

The *Piper guineense* stem referred to in this work was the climbing part of the plant when it climbed a tree to form a canopy or the sprawling portion when it could not get a tree to climb. The stem was sourced routinely from a plant growing in Igbaye (Osun State, Nigeria) and was taxonomically identified by Dr. H. C. Illoh (Dept. of Botany, Obafemi Awolowo University) who also kept a herbarium specimen, IFE Herb 264. The first collection was made in October, 1995. Freshly-collected plant material was dried in an aerated oven at 45 °C before communition to powder for chemical processing.

3.3. Extraction, isolation and identification procedures

For GC/MS investigations, pulverized whole stem (210 g) was covered with methanol (A.R. grade, 1 l.) with occasional shaking and extracted for 72 h. at RT. MeOH was removed under reduced pressure (bath temp. 40 °C) to leave a residue (4.61 gm). This residue was triturated in MeOH/H_2O (1 : 1) and filtered. The mixture was extracted with pentane and afterwards with $CHCl_3$. Each extract was washed with NaCl, dried over anh. Na_2SO_4, filtered and reduced to low volume. Samples of the residue from the pentane extract (630 mg) and $CHCl_3$ (1.04 g) were separately subjected to GC-MS analysis.

To isolate some constituents, pulverized whole stem (1.84 kg) was exhaustively extracted in MeOH for 96 h in the dark. MeOH was removed at reduced pressure (water bath temp. at 40 °C) to leave a residue (183.93 g). This residue was taken up in a MeOH/H_2O (1 : 1) mixture, filtered and extracted with $CHCl_3$ (500 ml × 3). The combined $CHCl_3$ extract was washed with NaCl, dried over anh. Na_2SO_4, filtered and concentrated to dryness, to leave a residue (46.80 g). Portions of this residue were chromatographed over silica gel (pTLC. S_iO_2 $60F_{254}$, IMM, Solv I.). A total of six fractions designated PgstO1-6 were obtained. The corresponding fractions were separately eluted in $CHCl_3$ and monitored by TLC and GC-MS. The concentration of some fractions resulted in some deposits of constituents which were purified further by crystallisation while others were re-chromatographed in solv. II. for further purification and isolation of constituents.

Alkaline hydrolysis: Compound in 10% alcoholic KOH was heated under reflux for 48–50 h and crystals in the form of K salt were collected by filtration, dissolved in minimum amount of H_2O and acidified with dil. HCl. Precipitates were usually extracted in $CHCl_3$ for further analysis. The alcoholic filtrates were usually acidified and evaporated to dryness before further purification and analysis.

Catalytic hydrogenation: Pd–C catalyst (20 mg) was usually added to the sample or mixture (200 mg) in dry MeOH (10 ml) at normal atmospheric conditions with the mixture stirred under N_2 and then H_2 until the uptake of H_2 was complete. The reaction mixture was filtered and evaporated *in vacuo* to yield the hydrogenated product which was also analysed by GC-MS and TLC.

Synthesis: Extensive syntheses were carried out following the procedure used earlier [6].

In this work and for most constituents of low to medium concentrations, structural determinations were based on their MS, hydrogenation products, chromatographic behaviour and comparison with synthetic analogues. For those at fairly high concentrations, we have relied, in addition to the above, on m.pt determinations, hydrolysis products and spectroscopic data. Retention times of synthetic compounds, compounds previously isolated by us and some locally-purchased products were compared with those of our isolates to confirm the structures. In four cases, we found it convenient to mix an authentic sample with an isolate to prove identity.

3.4. Analysis of constituents

The whole stem pentane extract representing about 13.7% of the total MeOH extract contained the volatile oil components – the terpenes, terpenoids, fatty acids, benzoic acid derivatives and many of the amides. Fractions Pgst05 and 06 also contained these compounds.

3.4.1. N-Pyrrolidyl-1-acetylamide (19)

Detected in Pgst01. GC: t_R = 16.28 min-EIMS (m/z, % int.): 113 (M^+, 73), 98 (CO-Pyrrolidyl, 100), 70 (Pyrrolidyl, 87), 84 (40), 55 (75). This new natural product is identical with a synthetic specimen obtained from the reaction of acetylchloride and pyrrolidine.

3.4.2. N-Piperidyl-1-acetylamide (33)

Detected as a minor component in Pgst01. GC: t_R = 19.04 min – EIMS (m/z, % int.): 127 (M^+, 80), 112 (CO-Piperidyl, 43), 84 (Piperidyl, 100), 70 (72), 56 (66), 67 (20), 85 (15). This new compound is identical with a synthetic specimen obtained from the reaction of acetylchloride and piperidine.

3.4.3. N-Isobutyl-2,4-octadienamide (1)

Detected from fraction Pgst05. GC: t_R = 40.63 min – EIMS (m/z, % int.): 195 (M^+, 42), 180 (M^+-CH_3, 45), 152 (M^+-C_3H_7, 56), 123 (M^+-N-isobutyl, 98), 113 (90), 96 (M^+-CO–N-isobutyl, 100), 81 (65), 67 (60). Catalytic hydrogenation produced N-isobutylcapramide, EIMS (m/z, % int.): 199 (M^+) for $C_{12}H_{25}NO$.

3.4.4. N-Isobutyl-2-decenamide (2)

Detected in fraction Pgst05 as a new product. GC: t_R = 45.43 min – EIMS (m/z, % int.): 225 (M^+, 12), 210 (M^+-CH_3, 38), 182 (M^+-$CH(CH_3)_2$, 45), 153 (M^+-N-isobutyl, 100), 154 (26), 126 (M^+-$CH_3(CH_2)_6$-, 69), 140 (M^+-$CH_3(CH_2)_5$-, 15), 69 (70). The strong ions at m/z, 126 and 140 confirm the position of the double bond in this new compound. Catalytic hydrogenation gave a product GC: t_R = 43.18 min, MS: 227 (M^+, 5), 115 (71), 100 (55), 172 (30), 128 (28), 184 (19), 72 (24), 60 (100), 142 (10).

3.4.5. N-Isobutyl-2,4-decadienamide (pellitorine) (3)

Detected in fraction Pgst05. GC: t_R = 48.15 min – EIMS (m/z, % int.): 223 (M^+, 34), 208 (M^+-CH_3, 40), 180 (M^+-$CH(CH_3)_2$ 124), 151 (M^+-N-isobutyl, 70), 152 (M^+-$CH_3(CH_2)_4$, – 59), 96 (100), 113 (75), 95 (73). Catalytic hydrogenation gave a product as with 2.

3.4.6. N-Piperidyl tetrahydrodecanamide (34)

Detected in fraction Pgst04. GC: t_R = 49.69 min – EIMS (m/z, % int.): 239 (M^+, 7), 127 (M^+-CO-Piperidyl, 100), 140 (M^+-$CH_3(CH_2)_5$-, 46), 112 (CO-Piperidyl, 60), 84 (Piperidyl), 70 (M^+-$(CH_2)_4$ CO-Piperidyl, 54), 154 (9), 99 (5), 69 (15). The compound behaved like a saturated aliphatic amide giving a base peak at m/z 127 arising from the fission of the bond beta to the carbonyl group, followed by McLafferty rearrangement.

3.4.7. N-Isobutyl-3,4-dimethoxybenzoic acid amide (14)

5 mg obtained from fraction Pgst04. GC: t_R = 51.54 min – EIMS (m/z), % int.): 237 (M^+, 6), 222 (M^+-CH_3, 59), 194 (10), 181 (55), 180 (40), 166 (62), 151 (45), 150 (25), 138 (40), 110 (100) Identical (IR, M.pt, TLC) with the synthetic product obtained from the reaction of isobutylamine and 3,4-dimethoxybenzoic acid.

3.4.8. N-Isobutyl-2,4-hendecadienamide (4)

Detected as a trace in Pgst05. GC: t_R = 51.80 min – EIMS (m/z, % int.): 237 (M^+, 21), 222 (M^+-CH_3, 23), 208 (M^+-CH_2CH_3, 25), 194 (M^+-$CH(CH)_2$, 13), 180 (M^+-$CH_2CH(CH_3)_2$, 32), 166 (M^+-N-isobutyl, 74), 151 (M^+-$CH_3(CH_2)_5$,95), 152 (25), 96 (100), 81 (70).

3.4.9. N-Piperidyl-2-decenamide (35)

Detected in Pgst02. GC: t_R = 51.94 min – EIMS (m/z, % int.): 237 (M^+, 5), 222 (M^+-CH_3, 2), 208 (M^+-C_2H_5, 7), 194 (M^+-$CH_3(CH_2)_2$, 8), 180 (M^+-$CH_3(CH_2)_5$-, 9), 84 (12), 138 (M^+-$CH_3(CH_2)_6$-, 100), 127 (M^+-CO-Piperidyl, 18). The strong ions at m/z, 138 and166 confirm the position of the double bond at C-2 for this new compound.

Catalytic hydrogenation gave a product identical with 34.

3.4.10. N-Pyrrolidyl-1-cinnamoylamide (23)

11 mg obtained from fraction Pgst02. GC: t_R = 52.69 min – EIMS (m/z, % int.): 201 (M^+, 100), 131 (M^+-CO-Pyrrolidyl, 90), 103 (for PhCH=CH, 87), 77 (Ph, 44), 70 (Pyrrolidyl, 35), 91 (55), 172 (25), 200 (33), 115 (14). New constituent, identical (UV, IR, NMR) with a synthetic.

3.4.11. N-Isobutyl-3-(3,4-methylenedioxyphenyl)propionamide (= dihydrofagaramide) (11)

10 mg obtained from Pgst02. GC: t_R = 53.04 min – EMIS(m/z,% int.): 249 (M^+, 25), 192 (M^+-$CH_2CH(CH_3)_2$, 95), 177 (M^+-N-isobutyl, 100), 145 (67), 137 (17), 117 (20), 89 (30), 193 (14). This is a first report of its occurrence as a natural product, Strong ions at m/z 177, 192, 249 and 137 confirm its structure. Identical (NMR, MS, TLC) with a synthetic.

3.4.12. N-Pyrrolidyl-2,4-decadienamide (20) – Iyeremide A

Obtained from fraction Pgst02. GC: t_R = 53.74 min – EIMS (m/z, % int.): 221 (M^+, 15), 98 (CO-Pyrrolidyl, 17), 150 (M^+-$CH_3(CH_2)_4$-, 100), 164 (M^+-$CH_3(CH_2)_3$-15), 178 (M^+-$CH_3(CH_2)_2$-, 20), 192 (15), 206 (M^+-CH_3,5), 151 (20), 70 (22). It is a new natural product, the pyrrolidine analogue of pellitorine (3) and it is being designated iyeremide A. Catalytic hydrogenation gave a product GCt_R = 48.49 min – EIMS {m/z, % int.} 225 (M^+, 3), 113 (100), 70 (66), 98 (30), 126 (40) as expected.

3.4.13. N-Piperidyl-2,4-decadienamide (36) – Iyeremide B

Obtained from fraction Pgst02. GC: t_R = 54.44 min – EIMS (m/z, % int.): 235 (M^+, 12), 206 (M^+-CH_3CH_2, 15), 192 (M^+-$CH_3(CH_2)_2$-, 100) 178 (M^+-CH_3CH_2-, 40) 164 (M^+-$CH_3(CH_2)_4$-, 72), 150 (M^+-Piperidyl, 45), 138 (M^+-$CH_3(CH_2)_4(CH{=}CH)$-, 62), 84 (Piperidyl, 75). This new compound is the piperidyl analogue of pellitorine (3) and it is designated iyeremide B. After catalytic hydrogenation identical with 34.

3.4.14. N-Isobutyl-2,4-dodecadienamide (5)

Detected in Pgst04. GC: t_R = 54.65 min – EIMS (m/z, % int.): 251 (M^+, 10), 236 (M^+-CH_3, 12), 179 (M^+-N-Isobutyl, 42), 152 (M^+ – $CH_3(CH_2)_6$–, 40), 113 (45), 96 (100), 81 (52), 166 (15). Catalytic hydrogenation gave a product with GCt_R = 49.96 min – EIMS {m/s, % int.}: 255 (M^+, 4), 60 (100), 115 (80), 100 (48), 128 (27), 200 (24),(17), 212 (10), 170 (8), 142 (8)

3.4.15. N-Isobutyl-2,4-tridecadienamide (6)

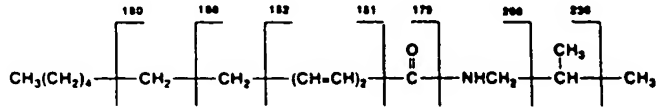
Obtained from Pgst05. GC: t_R = 59.72 min – EIMS (m/z, % int.): 265 (M^+, 14), 250 (M^+-CH_3, 16), 222 (M^+-$CH(CH_3)_2$, 15) 236 (M^+-CH_3–CH_2, 22) 209 (M^+-$CH_3CH(CH_3)_2$ + H, 18), 179 (M^+-CH_2-N-Isobutyl, 100), 166 (for $CH_3(CH_2)_7(CH{=}CH)_2$-, 80), 152 (M^+-$CH_3(CH_2)_7$-, 25), 138 (16) 127 (43), 110 (52). Catalytic hydrogenation gave a product, EIMS (m/z, % int.): 269 (M^+, 3), 268 (M^+-1.6), 256 (7), 115 (100), 60 (83), 100 (50), 128 (30), 72 (20), 142 (10), as expected.

3.4.16. N-Isobutyl-3,4-methylenedioxycinnamoylamide (= fagaramide) (13)

13 mg isolated from Pgst04. GC: t_R = 60.04 min – EIMS (m/z,% int.): 247 (M^+, 26), 190[M^+-$CH_2CH(CH_3)_2$, 100], 175 (M^+-N-isobutyl, 92), 145 (81), 117 (30), 89 (61), 63 (16), 232 (2). Previously isolated by us [20], identical (UV, IR, NMR) with an authentic sample. New constituent of the stem.

3.4.17. N-Pyrrolidyl-2,4-dodecadienamide (21)

Identified in Pgst02. GC: t_R = 60.09 min – EIMS (m/z, % int.): 249 (M^+, 8), 98[CO-Pyrrolidyl, 23), 150 (M^+-$CH_3(CH_2)_6$ – 100), 164 (M^+-$CH_3(CH_2)_5$-, 14), 178 (M^+-$CH_3(CH_2)_4$-, 17), 124 (6), 179 (M^+-Pyrrolidyl, 6), 113 (28), 70 (Pyrrolidyl, 20).



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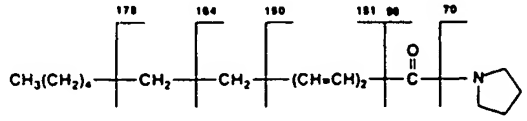

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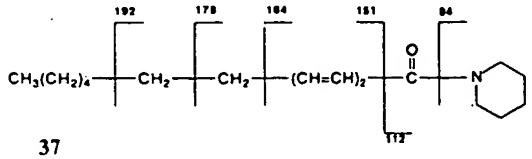


37

3.4.18. N-Pyrrolidyl-3-methoxycinnamoylamide (**24**)

4 mg isolated from Pgst02. GC: t_R = 60.38 min – EIMS (m/z, % int.): 231 (M^+, 25), 161 (M^+-Pyrrolidyl, 100), 162 (41), 163 (4), 133 (M^+-CO-Pyrrolidyl, 43), 131 (70), 118 (38), 103 ($PhOCH_3$, 28), 90 (30), 89 (21), 77 (15), 70 (80). Known natural product, identical with synthetic product and published data [13]. A new constituent in this plant.

3.4.19. N-Isobutyl-2,4-tetradecadienamide (**7**)

Identified in Pgst05. GC: t_R = 60.63 min – EIMS (m/z,% int.): 279 (M^+, 42), 264 (M^+-CH_3, 38), 236 (M^+-$CH(CH_3)_2$, 18), 207 (M^+-N-isobutyl, 62), 179 (8), 152 (M^+-$CH_3(CH_2)_8$-, 62), 96 (100), 113 (50), 166 (21), 180 (20). First report in this plant.

3.4.20. N-Piperidyl-2,4-dodecadienamide (**37**)

Identified as a minor component of the pentane fraction. GC: t_R = 60.67 min – EIMS (m/z,% int.): 263 (M^+, 10), 234 (M^+-CH_2CH_3, 8), 220 (M^+-$CH_3(CH_2)_2$-, 10), 192 (M^+-$CH_3(CH_2)_4$, 100), 178 (M^+-$CH_3(CH_2)$ – 41), 164 (for $(CH{=}CH)_2CO$- Piperidyl, 82), 151 (M^+-CO-Piperidyl, 12), 150 (38), 112 (15), 84 (86), 79 (53).

3.4.21. N-Isobutyl-5-(3,4-methylenedioxyphenyl)-2-pentenamide (= Δαβ-dihydropiperlonguminine) (**12**)

7 mg isolated from Pgst02. Identified as a minor component of the pentane fraction.
GC: t_R = 61.82 min – EIMS (m/z, % int.): 275 (M^+, 5), 218 (M^+-$CH_2CH(CH_3)_2$, 2), 203 (M^+-N-isobutyl, 2), 175 (M^+-CO–N-isobutyl, 16), 135 (M^+-$CH_2CH{=}CH{-}CO{-}$N-isobutyl, 100) 147 (2), 77 (20), 136 (10), 174 (17). Identical (UV, M.pt. IR, TLC) with an authentic sample. Known constituent [21] of the fruit. Hydrogenated product had GC_{iR} = 60.69 min – EIMS [(m/z, % int.): 277 (M^+, 30), 204 (86), 205 (27), 176 (45), 161 (20), 148 (100), 135 (70), 100 (20), 72 (18), 60 (45), 115 (25), 128 (18), confirming its structure.

3.4.22. N-Isobutyl-5-(3,4-methylenedioxyphenyl)-3-pentenamide (= Δβγ-dihydropiperlonguminine) (**15**)

Detected in Pgst02. GC: t_R = 62.11 min – EIMS (m/z, % int.): 275 (M^+, 20), 232 (M^+-$CH(CH_3)_2$, 2), 204 (M^+-N-isobutyl, 9), 176 (63), 175 (50), 140 (100), 161 (40, 135 (45), 131 (50), 117 (40), 116 (41), 115 (38), 103 (11). The strong ions at m/z 135 and 161 confirm the double bond in this isomer at C-3. First report as a natural product. Identical with the synthetic specimen published by Loder et al. [8].

3.4.23. N-Isobutyl-5-(3,4-Methylenedioxyphenyl)-2,4-pentadienamide (= piperlonguminine) (**16**)

It is a major component of Pgst03. 14 mg isolated. GC: t_R = 64.25 min – EIMS (m/z, % int.): 273 (M^+, 55), 230 (2), 217 (7), 216 (M^+-$CH_2CH(CH_3)_2$, 17), 201 (M^+-N-isobutyl, 56), 173 (M^+-CO–N-isobutyl, 78), 174 (40), 172 (30), 143 (45), 135 (44), 115 (100), 89 (12), 77 (12), 96 (10). Identified [16] previously from the fruit, after catalytic hydrogenation identical with the product from (**12**), known component [14] of *Zanthoxylum lemairie*.

3.4.24. N-Pyrrolidyl pentadecanoylamide (**22**)

GC: t_R = 64.71 min – EIMS (m/z, % int.): 296 (M^+ + 1, 40), 225 (M^+ – 2H-Pyrrolidyl, 70), 167 (for $CH_3(CH_2)_{11}$-, 25), 139 (for $CH_3(CH_2)_9$-,20), 195 (M^+-CO-Pyrrolidyl, 100), 70 (Pyrrolidyl, 12).

3.4.25. N-Pyrrolidyl-5-methoxy-3,4-methylenedioxycinnamoylamide (**28**)

Detected in the pentane extract. GC: t_R = 65.27 min – EIMS (m/z, % int.): 275 (M^+, 24), 276 (7), 205 (M^+-70, 4), 204 (30), 177 (M^+-CO-70, 5), 176 (32), 175 (14), 151 (3), 148 (58), 140 (14), 135 (60), 126 (44), 113 (100), 103 (17), 98 (37), 91 (26), 77 (50), 70 (57). After hydrogenation, gave a product at m/z 277 (M^+, 21), 165 (100), 166 (19).

3.4.26. N-Isobutyl-2,4-hexadecadienamide (**8**)

7 mg isolated from Pgst02. GC: t_R = 66.36 min – EIMS (m/z, % int.): 307 (M^+, 40), 292 (M^+-CH_3, 42), 264 (M^+-$CH(CH_3)_2$, 10), 235 (for $CH_3(CH_2)_{10}(CH{=}CH)_2CO$-, 70), 152 ($M^+$-$CH_3(CH_2)_{10}$, 100), 98 (96), 113 (82), 96 (80), 81 (67), 126 (35), 166 (25), 180 (22), 236 (20).
Isolated previously from the fruit. Catalytic hydrogenation gave a product. GC: t_R = 61.99 min – EIMS (m/z, % int.): 311 (M^+, 8), 268 (6), 256 (11), 239 (3), 226 (3), 184 (14), 170 (10), 142 (10), 128 (30), 115 (100), 100 (50), 72 (20), 60 (83).

3.4.27. N-Piperidyl pentadecanoylamide (**39**)

Detected in the pentane extract. GC: t_R = 66.40 min – EIMS (m/z, % int.): 308 (M^+-1, 30), 309 (M^+, 25), 226 (M^+-Piperidyl, 22), 224 (20), 195 (M^+-CO-Piperidyl, 53), 167{$CH_3(CH_2)_{11}$-, 53}, 139{$CH_3(CH_2)_9$-, 55}, 84 (Piperidyl, 100).

3.4.28. N-Piperidyl-5 (3,4-methylenedioxyphenyl)-pentanolamide (=tetrahydropiperine) (**45**)

Detected in Pgst04. GC: t_R = 66.50 min – EIMS (m/z, % int.): 289 (M^+, 63), 204 (93), 205 (5), 176 (26), 177 (4), 148 (65), 154 (40), 140 (40), 137 (100), 135 (32), 112 (76), 103 (16, 86 (53), 84 (52), 70 (91), 67 (37). First report as a natural product. Data identical with that published [8] for a synthetic specimen.

3.4.29. N-Piperidyl-2,4-tetradecadienamide (**38**)

Detected in Pgst04. GC: t_R = 66.57 min – EIMS (m/z, % int.): 291 (M^+, 8), 234 (M^+-$CH_3(CH_2)_3$-, 5), 206 (M^+-$CH_3(CH_2)_5$-, 24), 274 (M^+-CH_3, 10), 192 (M^+-$CH_3(CH_2)_6$-, 85), 178 ($CH_2(CH{=}CH)_2{-}CO$-Piperidyl, 28), 164 (M^+-$CH_3(CH_2)_8$- 70), 138 ($CH{=}CH{-}CO$-Pipridyl, 100), 112 (CO-Piperidyl, 32), 84 (Piperidyl, 90). Hydrogenated product had GC: t_R = 62.19 and major ions at m/z 295 (M^+, 3), 127 (100), 112 (60), 140 (33), 84 (35), 70 (37), 86 (18), 182 (6).

3.4.30. N-Pyrrolidyl-dimethoxycinnamoylamide (**27**)

5 mg isolated from fraction Pgst04. GC: t_R = 67.21 min – EIMS (m/z, % int.): 261 (M^+, 10), 191 (M^+-70, 55), 192 (100), 164 (M^+-CO-Pyrrolidyl, 67), 163 (28), 148 (35), 70 (37). Identical (UV, IR, NMR) with a synthetic specimen.

3.4.31. N-Piperidyl-5-(3,4-methylenedioxyphenyl)-2-pentenamide (= Δαβ-dihydropiperine) **(42)**

14 mg isolated, major component of Pgst03. GC: t_R = 67.66 min – EIMS (m/z, % int.): 287 (M^+, 15), 202 (M^+-Piperidyl-H, 45), 204 (26), 175 (M^+-CO-Piperidyl, 40), 174 (35), 144 (20), 148 (10), 135 (100), 138 (8), 112 (5), 84 (20), 77 (22). Catalytic hydrogenated product identical with **45** previously identified [12] from the fruit.

3.4.32. N-Piperidyl-5-(3,4-methylenedioxyphenyl)-4-pentenamide (= 4,5dihydropiperine) **(43)**

Detected in Pgst03. GC: t_R 67.69 min – EIMS (m/z, % int.): 287 (M^+, 10), 202 (M^+-H-Piperidyl, 20), 174 (M^+-CO-Piperidyl, 40), 175 (28), 135 (Methylenedioxybenzyl cation, 100), 127 (10), 161 (5), 144 (5), 116 (3), 77 (9), 84 (5), 86 (10). Identified [16] from the root. After catalytic hydrogenation identical with **45**.

3.4.33. N-Piperidyl-5-(3,4-methylenedioxyphenyl)-3-pentenamide (= Δβγ-dihydropiperine) **(44)**

Present in Pgst03. GC: GC: t_R 69.13 min – EIMS (m/z, % int.): 287 (M^+, 25), 204 (M^+-Piperidyl, 100), 202 (25), 174 (42), 176 (30), 148 (43), 144 (40), 84 (48), 115 (30), 135 (20), 166 (5). New natural product, fragmentation pattern similar to that published [8].

3.4.34. N-Pyrrolidyl-5-(3,4-methylenedioxyphenyl-2,4-pentadienamide (= trichostachine) **(25)**

11 mg obtained from Pgst02. GC: t_R = 69.93 – EIMS (m/z, % int.): 271 (M^+, 35), 272 (M^+ + 1,5), 201 (M^+-Pyrrolidyl, 66), 200 (25), 202 (20), 173 (M^+-CO-Pyrrolidyl, 40), 172 (28), 171 (25), 174 (18), 143 (30), 135 (27), 115 (100), 70 (Pyrrolidyl, 5). Identical (TLC, NMR) with an authentic sample. Known component of the fruit [15].

3.4.35. N-Piperidyl-5-(3,4-methylenedioxyphenyl)-2,4-pentadienamide (= piperine) **(46)**

10mg obtained from Pgst02. GC: GC: t_R = 70.41 min – EIMS (m/z, % int.): 285 (M^+, 23), 284 (M^+-1,5), 201 (M^+-Piperidyl, 51), 200 (15), 202 (14), 173 (37), 172 (30), 171 (24), 174 (24), 149 (45), 143 (42), 144 (20), 135 (15), 115 (100), 89 (14), 84 (11). Identical (TLC, NMR) with an authentic. Known component of the fruit [15].

3.4.36. N-Pyrrolidyl-5-(2-methoxy-4,5-methylenedioxyphenyl) -2-pentaenamide (= Δαβ-dihydrowisanidine) **(26)**

Detected in Pgst03. GC: t_R = 70.95 min, EIMS (mz,% int.): 303 (M^+, 4), 205 (M^+-CO-Pyrrolidyl, 4), 166 (10), 165 (M^+-CH=CH CO-Pyrrolidyl, 100), 135 (14), 107 (9), 79 (13), 77 (17), 70 (Pyrrolidyl, 4). Data identical with that published [17] for a sample obtained from the seeds.

3.4.37. N-Isobutyl-2,4-octadecadienamide **(9)**

Detected in Pgst05. GC: t_R = 71.23 min – EIMS (m/z, % int.): 335 (M^+, 50), 320 (M^+-CH_3, 52), 263 (M^+-N-isobutyl, 52), 208 (M^+-$CH_3(CH_2)_8$-, 9), 194 (M^+-$CH_3(CH_2)_9$-, 10), 180 (M^+-$CH_3(CH_2)_{10}$, 20), 166 (M^+-$CH_3(CH_2)_{11}$-, 25), 152 (for-(CH=CH)$_2$ CON-isobutyl,70), 113 (100), 98 (85), 81 (62), 115 (40), 336 (12). Hydrogenated product gave an M^+ at m/z 339 as expected. Known constituent [15] of the fruit.

3.4.38. N-Piperidyl-5-(2-methoxy-4,5-methylenedioxyphenyl) -2-pentenamide (= Δαβ-dihydrowisanine) **(47)**

4 mg obtained in Pgst03. GC: t_R = 71.58 min – EIMS (m/z, % int.): 317 (M^+, 8), 84 (Piperidyl, 2), 205 (M^+-CO-Piperidyl, 3), 165 (M^+-CH_2CH=CH–CO-Piperidyl, 100), 166 (10), 135 (12), 115 (2), 107 (7), 79 (8), 77 (9). Fragmentation pattern of **47** and its hydrogenated product. GC: t_R = 71.11 min, M^+ at m/z 319 (55) identical with published data [18] for an isolate from the roots.

3.4.39. N-Piperidyl-2,4-hexadecadienamide **(40)**

Detected in Pgst 04. GC: t_R = 71.67 min – EIMS (m/z, % int.): 319 (M^+, 10), 234 (M^+-Piperidyl, 9), 84 (Piperidyl, 59), 192 (M^+-$CH_3(CH_2)_8$-, 89), 178 (M^+-$CH_3(CH_2)_9$-, 39), 164[(CH=CH)$_2$CO-Piperidyl, 75], 206 (M^+-$CH_3(CH_2)_7$-, 16), 127 (28), 112 (CO-Piperidyl, 18). Yielded a hydrogenated product GC: t_R = 68.00 min and major ions at m/z 323 (M^+, 2), 127 (100), 112 (36), 70 (26), 140 (23), 84 (23), 86 (15).

3.4.40. Cyclopiperstachine **(17)**

Detected in Pgst 04. GC: t_R = 71.90 min – EIMS (m/z, % int.): 355 (M^+, 100), 282 (M^+-N-isobutyl-H,12), 284 (5), 255 (M^+-CO–N-isobutyl, 40), 254 (42), 256 (30), 257 (4), 247 (11), 240 (11), 220 (68), 201 (10), 152 (13), 148 (30), 135 (30), 121 (42), 115 (33), 91 (44), 103 (22), 79 (22). New constituent, fragmentation identical with literature [19]. Yielded a hydrogenated product with GC: t_R = 70, 02min and EIMS [m/z, % int]: 357 (M^+, 95), 287 (20), 222 (100), 225 (2), 135 (85), 123 (26), 72 (4) as expected.

3.4.41. N-Piperidyl-9-octadecenamide **(41)**

Detected in Pgst03 as a minor component. GC: t_R = 73.02 min – EIMS (m/z, % int.): 349 (M^+, 4), 84 (Piperidyl, 25), 86 (55), 127 ($CH_3(CH_2)_7$-, 100), 140 ($CH_3(CH_2)_7CH$=CH-, 45), 112 (CO-Piperidyl, 38), 154 (M^+-$(CH_2)_6$-CO-Piperidyl, 5), 264 (M^+-H-Piperidyl, 2). New natural product, hydrogenated product had a GC: t_R = 72.77 and major ions at 351 (M^+, 2), 182 (3), 140 (26), 127 (100), 112 (42), 86 (20), 84 (Piperidyl, 25), 70 (22) as expected.

3.4.42. N-Pyrrolidyl-5-(2-methoxy-4,5-methylenedioxyphenyl)-2,4-pentadienamide (= wisanidine = okolasin = 6-methoxytrichostachine) **(30)**

Detected in Pgst03). GC: t_R = 74.28 min – EIMS (m/z, % int.): 301 (M^+, 100), 231 (M^+-Pyrrolidyl, 87), 230 (50), 232 (40), 233 (5), 203 (M^+-CO-Pyrrolidyl, 27) 204 (18), 202 (32), 201 (60), 187 (16), 173 (80), 172 (35), 171 (21), 151 (12), 150 (12), 145 (90), 124 (20), 115 (65), 102 (31), 70 (17). Data identical with published information [13, 20].

3.4.43. N-Piperidyl-5-(2-methoxy-4,5-methylenedioxyphenyl)-2,4-pentadienamide (= wisanine = 2-methoxy piperine) **(48)**

Obtained from Pgst04. GC: t_R = 74.57 min – EIMS (m/z, % int.): 315 (M^+, 100), 284 (5), 231 (M^+-Pyrrolidyl, 61), 232 (61), 230 (40), 232 (7), 215 (10), 203 (M^+-CO-Piperidyl, 24), 204 (35), 201 (35), 202 (28), 187 (32), 178 (50), 173 (82), 171 (50), 163 (21), 145 (67), 129 (25), 115 (45), 84 (26). Fragmentation identical with that given for a sample isolated from the roots [3, 4]. Hydrogenated product had a GC: t_R = 71.11 min and major ions at m/z 319 (M^+, 55), 234 (48), 175 (100), 165 (55), 127 (56), 86 (23), 84 (6).

3.4.44. Cyclostachine B **(29)**

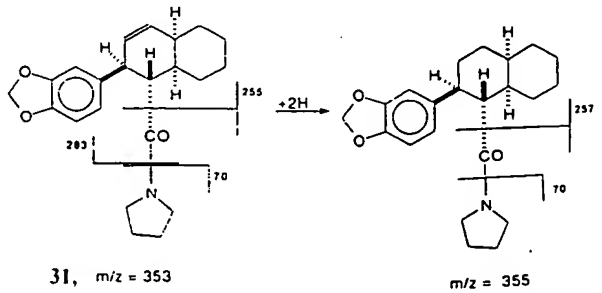
Detected also in Pgst04. GC: t_R = 74.94 min – EIMS (m/z, % int.): 353 (M^+, 50), 70 (Pyrrolidyl, 43), 254 (M^+-CO-Pyrrolidyl, 6), 252 (5), 323 (18), 242 (10), 228 (22), 218 (100), 135 (65), 98 (CO-Pyrrolidyl, 61), 55 (50), 72 (21), 124 (18), 150 (28), 152 (6). First report in this plant, MS identical with published data [9]. Yielded a hydrogenated product, GC: t_R = 74.40 min and EIMS (m/z, % int.): 355 (M^+, 97), 256 (100), 247 (27), 220 (40), 225 (27), 148 (90), 140 (83), 113 (43), 98 (47), 70 (37) as expected.

3.4.45. Cyclostachine A **(31)**

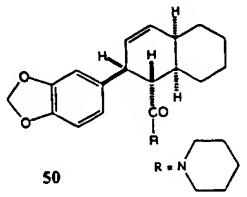
Present in Pgst04. GC: t_R = 75.19 min – EIMS (m/z, % int.): 353 (M^+, 100), 307 (23), 308 (16), 270 (25), 254 (M^+-CO-Pyrrolidyl, 30), 255 (19), 240 (20), 218 (58), 212 (35), 150 (31), 135 (55), 115 (52), 77 (40), 113 (40), 70 (Pyrrolidyl, 62). Yielded a hydrogenated product GC: t_R = 74.43 min and EIMS (m/z, % int.): 355 (M^+, 100), 257 (15), 256 (100), 246 (23), 225 (30), 220 (61), 113 (40) 135 (38), 70 (33), 98 (27), 148 (30).

3.4.46. Cycloguineense A **(50)**

Detected in Pgst04. GC: t_R = 75.47 min – EIMS (m/z, % int.): 367 (M^+, 100), 368 (M^+ + 1, 15), 337 (10), 282 (8), 254 (M^+-CO-Piperidyl, 31), 255 (11), 240 (34), 232 (76), 228 (34), 212 (12), 164 (27), 153 (12), 138 (30), 135 (46), 127 (25), 112 (65), 86 (25), 84 (Piperidyl, 36), 69 (28). This is a new natural product, the N-piperidyl derivative of cyclostachine A. The fragmentation follows the pattern postulated for cyclostachine with the piperidine moiety replacing the pyrrolidine moiety. Its hydrogenated product had GC: t_R = 75.72 min and major ions at m/z 369 (M^+, 75), 256 (100), 284 (15), 234 (40), 135 (62), 127 (61), 84 (13) as expected.



31, m/z = 353 m/z = 355



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3.4.47. N-Isobutyl-2,4-eicosadienamide (**10**)

Present in Pgst05. GC: t_R = 75.84 min – EIMS (m/z, % int.): 363 (M^+, 62), 348 (M^+-CH_3, 38), 320 (M^+-$CH(CH_3)_2$, 12), 291 (M^+-isobutyl, 51), 263[$CH_3(CH_2)_{14}(CH{=}CH)_2^+$, 5], 152[$M^+$ –N–$CH_3(CH_2)_{14}^+$, 100], 113 (95), 98 (70), 115 (70).
Data identical with published information on a sample isolated from the fruits [15, 19].

3.4.48. Cycloguineense B (**51**)

Compound was detected in Pgst04. GC: t_R = 76.20 min – EIMS (m/z, % int.): 367 (M^+, 100), 368 (M^++1,34), 337 (2), 324 (4), 284 (12), 254 (M^+-CO-Piperidyl, 85), 255 (29), 240 (20), 232 (60), 212 (17), 164 (19), 153 (13), 152 (13), 138 (12), 135 (65), 127 (25), 115 (25), 112 (65), 84 (Piperidyl,36), 69 (28). Isomeric to **50** eluted at GC: t_R = 75.47 min. A novel compound with piperidyl substituting for the pyrrolidine moiety in cyclostachine. Hydrogenated product had GC: t_R = 75.74 min and major ions at m/z 369 (M^+, 100), 257 (35), 256 (94), 234 (55), 127 (53) as expected.

3.4.49. N-Pyrrolidyl-7-(3,4-methylenedioxyphenyl)hepta-2,4,6-trienamide (1-piperettyl pyrrolidine) (**32**)

Detected in Pgst04. GC: t_R = 82.31 min – EIMS (m/z, % int.): 297 (M^+, 33), 227 (M^+-70,20), 226 (41), 225 (21), 199 (M^+-CO-Pyrrolidyl, 23), 197 (16), 196 (12), 200 (12), 169 (65), 168 (15), 141 (100), 139 (20), 115 (81), 98 (14), 70 (14). A new constituent of this plant, the hydrogenated product had a GC: t_R = 70.97 min and major ions at m/z, 303 (M^+, 10), 168 (25), 148 (16), 135 (53), 126 (56), 113 (100), 98 (28), 72 (27), 70 (35) behaving like a saturated aliphatic amide with strong peaks at 113 and 126 from the fission of the bond β to the carbonyl group and H_2 transfer (McLafferty rearrangement). Also prominent was the tropylium ion at m/z 135 at the expense of the acyl ion.

3.4.50. N-Piperidyl-7-(3,4-methylenedioxyphenyl)-hepta-2,4,6-trienamide (= piperettine) (**49**)

Obtained from Pgst03. GC: t_R = 83.79 min – EIMS (m/z, % int.): 311 (M^+, 20), 227 (M^+-84,24), 226 (72), 225 (13), 199 (M^+-CO-Piperidyl, 40), 198 (20), 200 (10), 176 (13), 169 (66), 168 (9), 141 (100), 139 (25), 135 (9), 115 (77), 112 (15), 102 (5), 86 (11), 84 (23). A new constituent, it gave a hydrogenated product GC: t_R = 72.23 min and major ions at m/z, 317 (M^+, 12), 232 (4), 182 (32) 148 (28), 140 (62), 135 (56), 127 (100), 112 (56), 86 (40), 84 (26), 77 (30), 70 (33), 60 (18) as expected.

3.4.51. N-Isobutyl-13-(3,4-Methylenedioxyphenyl) trideca-2,4,12-trienamide (= guineense) (**18**)

Obtained from Pgst04. GC: t_R = 94.65 min – EIMS (m/z, % int.): 383 (M^+, 13), 311 (M^+-72, 3), 283 (M^+-CO-N-isobutyl, 6), 282 (7), 285 (4), 261 (8), 249 (10), 248 (100), 211 (10), 201 (14), 148 (27), 149 (23), 161 (17), 135 (43), 131 (42), 103 (48), 77 (22). Previosly isolated from the fruit [16], the hydrogenated product had a GC: t_R = 82.30 min and major fragments at m/z 389 (M^+, 51), 359 (4), 254 (10), 135 (100), 127 (42), 115 (61), 100 (20), 60 (20) as expected.
The lignan sesamin- GC: t_R = 80.33 min – EIMS (m/z, % int): 354 (M^+, 18), 323 (3), 219 (6), 178 (11), 161 (23), 150 (30), 149 (100), 148 (45), 135 (26), 131 (21), 121 (20), 77 (17), 65 (13) and the sterols campesterol – GC: t_R = 82.60 min – EIMS (m/z, % int): 400 (M^+, 100) for $C_{28}H_{48}O$; stigmasterol – GC: t_R = 83.81 min – EIMS (m/z,% int): 412 (M^+, 100) for $C_{29}H_{48}O$; and sitosterol – GC: t_R = 85.93 min – EIMS (m/z, % int): 414 (M^+, 100) for $C_{29}H_{50}O$ were also identified from the stem.

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